(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
5 December 2002 (05.12.2002)

PCT

(10) International Publication Number
WO 02/097189 A1

(51) International Patent Classification[7]: D21C 11/00, C02F 5/02 // 103:28

(21) International Application Number: PCT/FI02/00463

(22) International Filing Date: 30 May 2002 (30.05.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
20011131 30 May 2001 (30.05.2001) FI

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(81) Designated States *(national)*: AE, AG, AL, AM, AT (utility model), AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ (utility model), CZ, DE (utility model), DE, DK (utility model), DK, DM, DZ, EC, EE (utility model), EE, ES, FI (utility model), FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK (utility model), SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 02/097189 A1

(54) Title: A METHOD FOR TREATING CIRCULATION WATERS

(57) Abstract: The present invention relates a method for the treating of circulation waters in papermaking processes wherein a stream of process water separated from an aqueous cellulosic pulp suspension of the papermaking process is provided, said separated process water having an elevated level of free calcium ions. A pH of not less than pH 9 is provided in the process water. Gaseous carbon dioxide is distributed in the process water in an amount sufficient for precipitating a substantial part of the calcium ions as solid calcium carbonate in the water and for obtaining a decreased level of free calcium ions in the water. The calcium ion depleted process water is returned to the papermaking process, thereby reducing or preventing the accumulation of calcium ions circulating in the process.

A method for treating circulation waters

The present invention relates to the treating of circulation waters in papermaking.

Calcium carbonate $CaCO_3$ is commonly used in paper making as a filler or pigment because it has a high brightness. It is also very white and can be purchased at reasonable prices. The calcium carbonate may be naturally occurring chalk or calcite or it may be synthetically produced precipitated calcium carbonate (PCC). It is well known in the art that the calcium carbonate dissolves in acids and the more acid is present the better the dissolution is. Calcium carbonate is sparingly soluble in alkaline conditions above a pH of about 8, but it is attacked by acids such as sulfuric acid and alum, as a result of which it is solubilized. According to literature (D. Eklund, T. Lindström, Paper Chemistry - an introduction, DT Paper Science Publications, Grankulla, Finland 1991, p. 253) an increase in the carbon dioxide partial pressure increases the solubility of calcium carbonate. This can be presented with the following equation:

(1) $CaCO_3 + CO_2 + H_2O \leftrightarrow Ca(HCO_3)_2$

A part of the calcium carbonate used as a filler in the paper machine dissolves into the process waters because of for example the pH gradients between the mass and the circulation waters, acidic additive chemicals or acids caused by microbiological activity. Some calcium is also provided with the wood. Dissolved calcium reacts for example with extracts causing harmful precipitates.

Calcium carbonate is sparingly soluble in water but dissolves at pH below 8. For calcium carbonate in water the following equations can be written:

(2) $CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$
(3) $CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + OH^-$
(4) $CaCO_3 + 2\,H^+ \leftrightarrow Ca^{2+} + CO_2 + H_2O$

At a pH below about 8 the dissolution of calcium carbonate and consequently the concentration of free calcium ions increases and foaming may be observed as carbon dioxide gas is released according to equation (4). In the papermaking processes calcium carbonate is added as a filler to the stock prior to paper formation and consequently a part of the filler particles will enter the process waters circulating in the papermaking system. With the use of closed circulating waters in the papermaking system, the solubilization of calcium carbonate causes accumulation of high concentrations of calcium ions which cause complex problems in

the papermaking. Among these problems there may be mentioned coagulation of sticky particles, soap and ink particles; precipitation of inorganic calcium salts as a scaling; precipitation of calcium oxalate and reprecipitation of calcium carbonate; interference with retention aids, dispersants and other charged paper additives; etc. When calcium carbonate is used as a pigment in coated papers, a part of the calcium carbonate will be recirculated to the process with the broke.

If the pulp or stock is acidified with sulfuric acid and the short circulation is run at an acidic pH, calcium carbonate filler will be dissolved in the circulating water, the amount of circulating calcium ions will accumulate in the water and various precipitation and foaming problems will occur.

Recycled waste paper as well as broke (herein generally referred to as recycled fibers) may contain calcium carbonate as filler and/or pigment. The repulping of recycled fibers is generally performed at an alkaline pH wherein the calcium carbonate remains essentially in solid form. However, if the paper machine is run at an acidic, neutral or pseudoneutral pH range, the calcium carbonate deriving from the recycled fibers will start to dissolve.

Through the stock preparation and the short circulation a number of paper chemicals and dilution waters are added, some of which are acidic and therefore decrease the pH of the pulp. At each acidic addition calcium carbonate may be lost and there may be foaming problems due to a decomposition of dissolving calcium carbonate.

Carbon dioxide is a gas, which easily dissolves in water or a pulp suspension forming carbonic acid and/or bicarbonate ions according to the reaction:

(5) $CO_2 + H_2O <\!\!\!-\!\!\!> H_2CO_3 <\!\!\!-\!\!\!> H^+ + HCO_3^-$

At a high pH, especially greater than 10, the predominant reaction is

(6) $CO_2 + 2\ OH^- <\!\!\!-\!\!\!> CO_3^{2-} + H_2O$

WO99/00545 describes a method of reducing the content of calcium in a pulp suspension by alkalizing the pulp suspension to a pH above 8 and adding carbonate ions to the pulp suspension in an amount of at least 0.1 kg carbonate ions by the ton pulp for formation of calcium compounds which are adsorbed on the pulp. Calcium is transferred from the liquid phase to the pulp fibers. The consistency lies suitably within the interval from 8 to 16 %. The invention does not relate to circulation waters.

According to EP1008561 calcium hardness of recycled paper-processing water is controlled by precipitating calcium ion in process water into calcium carbonate through addition of sodium carbonate or sodium hydrogen carbonate to white water short-circulated in a papermaking process and removing the calcium carbonate precipitate from the water. Air or carbon dioxide may be used for removal of the precipitate by flotation.

US 3,639,206 describes removal of ligneous colour bodies and suspended fibrous material, whereby waste water effluent is treated first with a calcium salt (CaO, $Ca(OH)_2$). The separated aqueous phase is then contacted with CO_2 gas to precipitate any dissolved calcium salts and a final separation is performed.

US 5,679,220 discloses a method enhancing the deposition and retention of particulate filler on papermaking fibers wherein separate slurries of fibers and $Ca(OH)_2$ or equivalent thereof are combined with gaseous precipitant (CO_2) to form *in situ* calcium carbonate on the fibers.

According to GB Patent Application 2 008 562 carbon dioxide may be used for increasing the solubility of calcium carbonate and for the hardening of recycled waters used in the treatment of pulp from waste paper.

According to US Patent 5,262,006 precipitation of gypsum in an alkaline recycle or broke derived pulp may be prevented by adding carbon dioxide to form bicarbonate ions in the alkaline pulp and to precipitate calcium as carbonate.

According to WO 99/35333 and WO 99/45202 the dissolution of calcium carbonate in a papermaking system is reduced by the addition of carbon dioxide to the pulp as the pH goes below 8. The accumulation of calcium ions in the system is reduced since less calcium ions enter the system.

According to WO 98/56988 the pH of a pulp suspension in the stock preparation of a paper machine is stabilized by carbon dioxide. A combination of sodium hydroxide and carbon dioxide provide a significant buffering effect in the pulp. The stabilized pH reduces the dissolution of calcium carbonate at acidic addition points.

Despite all precautions taken by paper makers, some of the solid calcium carbonate in the papermaking system tends to end up in the circulating waters.

Closed circulating water systems are used more and more in order to lower the amount of

water discharged from the papermaking process. In the closed systems the accumulating calcium ions that cannot be cleared from the circulation waters by conventional methods, such as membrane filtration, disturb the process at an ever increasing level.

Since the accumulating calcium ions in the circulating waters cause many problems in the papermaking, there is a need for a method to clean the circulation waters of the calcium ions.

The method according to the present invention enables *in situ* cleaning of the circulation waters. The method is defined in the appended claims, the contents of which form a part of this specification.

Thus, the present invention relates to a method for the treating of process water circulating in a papermaking process. The method comprises the steps of providing a stream of process water separated from an aqueous cellulosic pulp suspension in a first unit operation of said papermaking process, said separated process water having an elevated level of free calcium ions; providing in said process water, without the addition of calcium oxide or hydroxide, a pH of not less than pH 9; distributing gaseous carbon dioxide in said process water in an amount sufficient for precipitating a substantial part of said calcium ions as solid calcium carbonate in said water and for obtaining a decreased level of free calcium ions in said water; optionally removing solid calcium carbonate from said process water; and returning the resulting calcium ion depleted process water to said papermaking process at a second unit operation; thereby reducing or preventing the accumulation of calcium ions circulating in said papermaking process.

The present invention provides a cleaning station, i.e. a kind of kidney in the circulating process waters. The kidney removes the excess calcium ions and solves the problems caused by the elevated levels of calcium ions in the papermaking process. It enables the paper maker to continuously circulate the same waters without disturbing calcium precipitations.

In the prior art most of the attempts at removing free calcium ions have been performed with the fibers present in the liquid. This has had the benefit of precipitating the calcium carbonate directly onto the fibers. However, some cellulosic fibers are sensitive to variations in pH. It is also difficult to know the amount of filler precipitated onto the fibers in this way. Sometimes it is not desirable to have the calcium carbonate precipitate on and in the fiber itself.

Sodium bicarbonate has also been used in the prior art in order to remove calcium. The addition of sodium bicarbonate e.g. as a slurry may be complicated and the pH will adjust itself only to about 8. The addition of carbon dioxide as disclosed by the present invention can

be performed more flexibly into the process in a desired part of the process.

The present invention also concerns a process for producing paper in a papermaking system. The process comprises the steps of providing an aqueous cellulosic pulp suspension in said papermaking system; causing free calcium ions to be present in said aqueous cellulosic pulp suspension; in a first unit operation of said papermaking system, separating process water having an elevated level of free calcium ions from said aqueous cellulosic pulp suspension; providing in a stream of said separated process water, without the addition of calcium oxide or hydroxide, a pH of not less than pH 9; distributing gaseous carbon dioxide in said stream of process water in an amount sufficient for precipitating a substantial part of said free calcium ions as solid calcium carbonate in said water, for obtaining a decreased level of free calcium ions in said water; optionally removing solid calcium carbonate from said stream of process water; returning the resulting calcium ion depleted process water to said papermaking system at a second unit operation, to provide an aqueous cellulosic pulp suspension having a decreased level of free calcium ions; and processing said pulp suspension in said papermaking system into paper.

In the present invention process waters are separated from the pulp suspension and cleaned from calcium ions separately from the pulp suspension. The separation takes place in one unit operation and the calcium ion depleted waters are reintroduced into the process at another unit operation in the system. The stream of process water to be treated may comprise the whole or part of the waters separated from the pulp suspension in the first unit operation.

A typical first unit operation of the invention is the dewatering of a pulp suspension in the web forming section of a paper machine. Especially in cases where strong acids such a sulfuric acid have been used in a calcium carbonate filler process, the water drained through the wire contains elevated amounts of calcium ions. If these calcium ions are not removed from the water, the calcium ion level increases for each loop that the water makes. The circulation or loop that the separated water makes is generally called short circulation or long circulation. The present invention is applicable to both types of process waters.

The short circulation water is used in a second unit operation which comprises the dilution of the stock just before it is made into paper. The long circulation water may be used in various unit operations upstream in the process for purposes which are well known to those skilled in the art.

Calcium ion containing waters may also be found in other unit operations or clear filtrates and the calcium ion depleted water may be returned to the same or to another unit operation in the

papermaking process.

The "elevated level" of calcium ions as used in the present specification and claims is intended to mean any amount of calcium ions which is detrimental to the process. The acceptable level of calcium ions will vary greatly with the process as those skilled in the art know. For instance in the short circulation waters levels of about 100 mg Ca++/l may be acceptable, while severe problems may be caused if the calcium ion concentration rises above 150 mg/l or 200 mg/l.

In some process waters in a paper mill, e.g. spray waters, a substantially total freedom from calcium ions is required.

The extent to which the calcium ions are removed from the process waters depends on the pH of the treated water. In some cases the process water which is provided in the process and which is treated by the steps of the process will initially have a pH of not less than 9 and the kidney may function satisfactorily at such a pH. However, it is generally preferred to use a higher pH such as a pH above 10, or most preferably above 11. Calcium carbonate is precipitated more readily the higher the pH is. Therefore, in a preferred embodiment of the invention a pH which is higher than pH 9, and which is preferably 10 to 11 is provided in the process water.

The desired pH of the process water may be provided by adding an alkaline compound such as sodium or potassium hydroxide. It is not in accordance with the concept of the present invention to raise the pH with lime, i.e. calcium oxide or calcium hydroxide since these compounds add to the calcium ion content of the water. In the present invention the intention is to remove the calcium ions existing in the separated process waters as a precipitate. The idea is not, as in many prior art operations, to obtain as much solid calcium carbonate as possible.

The gaseous carbon dioxide which is used according to the invention is a gas which contains a substantial amount of carbon dioxide such that it will effectively achieve the object of precipitating calcium carbonate in the environment. The gas preferably contains at least 20 %, preferably more than 50 %, most preferably more than 90 % carbon dioxide. The gas may include other components which are not detrimental to the purpose of the gas in the invention and it may be, for instance flue gas containing carbon dioxide and sulfur dioxide.

In processes where calcium carbonate is used as a filler, the separated process waters may contain small amounts of solid calcium carbonate. Such solid calcium carbonate may improve

the operation of the kidney in that the small solid particles act as seeds or growth centers for the calcium carbonate precipitating from the liquid. It may, in fact, be useful to add a small amount of finely ground solid calcium carbonate to the process water after the separation step to ascertain that there are sufficient amounts of seeds in the solution. Such additional calcium carbonate should not be added at a pH lower than 8.

The addition, if any, of an alkaline compound as well as the addition of carbon dioxide is monitored mainly by pH. Thus, if sodium hydroxide has been used to raise the pH to 11, carbon dioxide or a carbon dioxide containing gas would generally be used to lower the pH to about 9 or below. For many purposes it is desirable to lower the pH of the water to a pH level of 8.5 to 6.0. Preferably the pH is lowered to pH 8.0 to 6.5, most preferably pH 7.5 to 7.0. Another acid than carbon dioxide may be used for lowering the pH below 9, but the use of carbon dioxide is preferred. Strong acids such as sulfuric acid may dissolve the precipitated calcium carbonate and should thus be avoided at least at pH below 8.

Care should be taken to add sufficient carbon dioxide to provide a proper precipitation of the calcium as carbonate. The proper functioning of the precipitation may be monitored by measuring the amount of free calcium ions in the in and out going waters. A substantial part of the calcium ions should be removed in the form of calcium carbonate so that an increased accumulation of calcium ions can be avoided. It is not possible to remove all calcium ions from the solution but a person skilled in the art will know the degree of calcium ion concentration acceptable in the process in question and will be able e.g. by raising the pH to a higher level and by subsequently adding more carbon dioxide to increase the precipitation and to provide a desired depletion of calcium ion from the water.

In the case where a higher pH is to be provided in the process water an alkaline compound is introduced first, for instance in a pipe or in a small mixing tank. Thereafter the carbon dioxide is added. The addition of carbon dioxide generally requires a pressurized addition point and therefore a suitable point is after a pump in a pipe line or in a pressurized tank or reactor. The precipitation of calcium carbonate starts immediately when the carbon dioxide contacts the calcium ion containing alkaline liquid. In some cases it may be desirable to feed the carbonated liquid to a tank for providing a sufficient retention time for the calcium carbonate particles to grow. Since the solubility of calcium carbonate decreases with rising temperatures, it may be useful to treat the process water at an elevated temperature. However, for energy consumption reasons heating of the vast amounts of waters is generally not economically feasible.

The precipitated calcium carbonate may be removed from the water by conventional means

such as by filtration or it may be left in the water for acting as a precipitated filler in the subsequent paper making. In any case, the treated water has a decreased concentration of calcium ions and when it is subsequently returned to the process at a second unit operation, such as dilution, washing etc. there will be no problems with calcium precipitation etc.

In the following the present invention will be illustrated by some examples which describe some embodiments of the invention. The Examples are not intended to restrict the scope of the invention. It is evident to a person skilled in the art that the invention can be carried out in a great variety of ways.

Example 1

In a partly integrated paper mill bales of fully bleached kraft market pulp were slushed at a pH of about 11. Paper making chemicals and sulfuric acid were added to the slushed pulp suspension to bring the pH of the pulp to a pH of about 7, which pH was maintained in the short circulation of the paper machine.

Calcium carbonate was added as filler and the white water contained dissolved calcium carbonate which gradually caused the calcium ion content to accumulate to elevated levels (over 200 mg Ca^{2+}/l). Precipitations of calcium salts and sticky particles occured in the process.

A kidney was installed in the white water circulation system. The pH of the circulation water was raised to a level of about pH 11 with NaOH. Then CO_2 was added to the water to cause precipitation of the calcium as calcium carbonate. The amount of dissolved calcium decreased from a level of 210 mg Ca^{2+}/l to a level of 110 mg Ca^{2+}/l. CO2 was added until a pH of about 8 had been reached. The water was returned to the process at this pH. The formed calcium carbonate followed the paper produced in the paper machine out from the process.

Example 2

A paper mill uses a pulp suspension consisting of a blend of de-inked pulp (DIP) and thermomechanical pulp (TMP). The pulp contains a significant amount of calcium carbonate deriving from the waste paper. The pH of the stock is adjusted to pH 6.8 to 6.9 with sulfuric acid and the paper machine is run at this pH.

Even though no calcium carbonate is added to the pulp as a filler, calcium ions accumulate in the circulating waters. The dissolved calcium reacts with organic particles in the pulp and

forms sticky precipitates in the paper and on the equipment.

In order to improve the process, a kidney in accordance with the invention is adopted in the system and the short circulation waters are treated first by raising the pH to 10 with sodium hydroxide and then by adding carbon dioxide to the water until the pH has decreased to 8. A part of the precipitated calcium carbonate is removed by sedimentation in a tank. Additional carbon dioxide is then added to the water to bring the pH back to 6.8 to 6.9.

As a result of the removal of the calcium ions from the water, the accumulation of calcium ions stops and there are no longer problems caused by calcium precipitations.

Claims

1. A method for the treating of process water circulating in a papermaking process, characterized by the steps of

- providing a stream of process water separated from an aqueous cellulosic pulp suspension in a first unit operation of said papermaking process, said separated process water having an elevated level of free calcium ions,

- providing in said process water, without the addition of calcium oxide or hydroxide, a pH of not less than pH 9,

- distributing gaseous carbon dioxide in said process water in an amount sufficient for precipitating a substantial part of said calcium ions as solid calcium carbonate in said water and for obtaining a decreased level of free calcium ions in said water,

- optionally removing solid calcium carbonate from said process water, and

- returning the resulting calcium ion depleted process water to said papermaking process at a second unit operation,

thereby reducing or preventing the accumulation of calcium ions circulating in said papermaking process.

2. A method according to claim 1, wherein said pH of not less than 9 is provided by adding an alkaline compound to a process water stream having an initial pH below 9.

3. A method according to claim 1 or 2, wherein said pH of not less than 9 comprises a pH of more than 9, preferably more than 10, most preferably more than 11.

4. A method according to claim 1, 2 or 3, wherein an increased pH of said process water is provided by the addition of sodium hydroxide to said process water.

5. A method according to claim 1, wherein carbon dioxide is distributed in said process water in order to lower the pH of said water below pH 9.

6. A method according to claim 1, wherein the carbon dioxide comprises a gas containing at least 20 %, preferably more than 50 %, most preferably more than 90 % carbon dioxide.

7. A method according to claim 2, wherein the pH is lowered to a level of 8.5 to 6.0, preferably 8.0 to 6.5, most preferably 7.5 to 7.0.

8. A method according to claim 1, wherein said process water contains small amounts of solid calcium carbonate.

9. A method according to claim 1, wherein solid calcium carbonate is added to the process water after the separation step.

10. A method according to claim 1, wherein said process water comprises water in the short circulation or the long circulation of a paper machine.

11. A method according to claim 1, wherein said process water comprises clear filtrate.

12. A method according to claim 1, wherein said carbon dioxide is distributed into said process water in connection with a pump in a pipe line.

13. A process for producing paper in a papermaking system, c h a r a c t e r i z e d in
- providing an aqueous cellulosic pulp suspension in said papermaking system,
- causing free calcium ions to be present in said aqueous cellulosic pulp suspension,
- in a first unit operation of said papermaking system, separating a stream of process water having an elevated level of free calcium ions from said aqueous cellulosic pulp suspension
- providing in a stream of said separated process water, without the addition of calcium oxide or hydroxide, a pH of not less than pH 9,
- distributing gaseous carbon dioxide in said stream of process water in an amount sufficient for precipitating a substantial part of said free calcium ions as solid calcium carbonate in said water, for obtaining a decreased level of free calcium ions in said water,
- optionally removing solid calcium carbonate from said process water,
- returning the resulting calcium ion depleted process water to said papermaking system at a second unit operation, to provide an aqueous cellulosic pulp suspension having a decreased level of free calcium ions, and
- processing said pulp suspension in said papermaking system into paper.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 02/00463

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: D21C 11/00, C02F 5/02 // C02F 103:28
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: D21C, C02F, D21F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI DATA, EPO-INTERNAL, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 9945192 A1 (KEMIRA KEMI AB), 10 Sept 1999 (10.09.99), page 4, line 21 - line 28; page 5, line 4 - line 25, abstract --	1-13
X	WO 9900545 A1 (SUNDS DEFIBRATOR INDUSTRIES AB), 7 January 1999 (07.01.99), page 3, line 11 - line 20; page 3, line 30 - line 36, claims 1,4, abstract --	1-13
X	JP 10174979 A (HITACHI ZOSEN CORP), 30 June 1998 (30.06.98) -- --------	1-13

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search	Date of mailing of the international search report
21 August 2002	05 -09- 2002
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Nina Bergström/ELY Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

Information on patent family members

06/07/02

International application No.
PCT/FI 02/00463

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9945192 A1	10/09/99	AU 734281 B	07/06/01
		AU 2445299 A	20/09/99
		AU 7091498 A	13/11/98
		BR 9808946 A	01/08/00
		BR 9908430 A	31/10/00
		CA 2322209 A	10/09/99
		CN 1292053 T	18/04/01
		EP 1011969 A	28/06/00
		EP 1060306 A	20/12/00
		JP 2002506134 T	26/02/02
		NO 20004187 A	22/08/00
		PL 342616 A	18/06/01
		SE 9800645 D	00/00/00
		SE 9803384 A	03/09/99
		US 6290812 B	18/09/01
WO 9900545 A1	07/01/99	SE 511794 C	29/11/99
		SE 9702512 A	31/12/98
JP 10174979 A	30/06/98	NONE	